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# Performance of a Robotic Weighing System and Quality Practices for Gravimetric Mass Measurements

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## ABSTRACT

Gravimetric analysis is an essential baseline measurement for air quality monitoring networks to monitor particulate matter and to track adherence to the National Ambient Air Quality Standards. The Clean Air Act requires the state and local agencies to monitor and report particulate matter concentrations as a part of their air monitoring requirements. High-throughput gravimetry laboratories need to be capable of weighing thousands of filter-based samples each month while maintaining strict quality control requirements set by the Federal Reference Method for the determination of particulate matter in ambient air.

Here, we present an evaluation of the performance of a robotic weighing system and review quality control measures applicable to gravimetric mass measurements. Results from this study show robotic weighing is better able to control static effects common to manual weighing. Electrostatic charges are increased with each human movement during the manual weighing process and, as indicated here, can occur suddenly and be difficult to detect. This study provides insights into the ability of robotic weighing to mitigate this effect and suggests new quality practices to detect and track the static effect.

***Keywords:*** Gravimetric mass; PM; Static; Quality Assurance; Robotic weighing system.

## INTRODUCTION

Airborne particulate matter (PM) contributes to public health and environmental concerns such as cardiovascular and respiratory health effects as well as decreased visibility and acid rain. PM consists of multiple chemical species present together. Fine particles with an aerodynamic diameter of 2.5 micrometers (µm) or less ($PM_{2.5}$), in particular, have been linked to adverse health impacts such as cardiovascular (Pope *et al.*, 2004; Henneberger *et al.*, 2005; Namdeo and Bell, 2005; Pope and Dockery, 2006; Vallejo *et al.*, 2006; Neuberger *et al.*, 2007; Bell *et al.*, 2008; Ren and Tong, 2008; Atkinson *et al.*, 2014; Grahame *et al.*, 2014) and respiratory diseases (Vedal, 1997; Pope and Dockery, 2006; Ren and Tong, 2008; Delfino *et al.*, 2009; Sinclair *et al.*, 2013; Atkinson *et al.*, 2014; Jones *et al.*, 2014). While specific components of $PM_{2.5}$ are believed to be important drivers of health effects (Grahame *et al.*, 2014), particularly of short-term health effects (Rohr and Wyzga, 2012), it is still unclear whether any single component is responsible for the health effects, or whether the species serve as an indicator for other pollutants (Rohr and Wyzga, 2012). Similarly, a recent review concludes that more research is needed to link specific PM components to long-term health impacts (Wyzga and Rohr, 2015). Additional research is also needed to determine whether combinations of certain species elicit adverse health responses. Gravimetric mass of PM therefore continues to be an important surrogate of regulatory importance linking particulate pollution to health and environmental impacts. As a result, the U.S. Environmental Protection Agency (EPA) has set National Ambient Air Quality Standards (NAAQS) for PM mass to protect human health and the environment. The Clean Air Act (CAA) requires the state and local agencies to monitor PM as well as to develop an emission reduction plan to meet the NAAQS if the NAAQS are not met.

Gravimetric analysis is an essential baseline measurement for air quality monitoring networks to track adherence to the NAAQS. Monitoring agencies rely on precise analysis methods to accurately report PM levels. To facilitate this analysis, the EPA has established a Federal Reference Method (FRM) that sets requirements for the collection and gravimetric mass analysis of PM.

The FRM methods for $PM_{10}$ (U.S.EPA, 2012a) updated in 2012 and $PM_{2.5}$ (U.S.EPA, 1997, 2012b) include collecting airborne PM on a suitable tared (i.e., pre-weighed) collection medium, such as a Teflon® membrane filter, by drawing air through a $PM_{10}$ or $PM_{2.5}$ inlet at a designated flow rate for a 24-hour sampling period. The loaded filter is subsequently

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reweighed to determine the net mass loading of collected PM. The mass concentration of PM in the ambient air is calculated from the net mass loading and the volume of air sampled, expressed typically in micrograms per cubic meter of air (µg $m^{-3}$). So, the gravimetric mass measurement is a simple process that basically involves weighing a Teflon® filter both prior to, and after, a defined sample collection event. However, the seemingly simple gravimetric analysis procedure is subject to influence from multiple factors including laboratory effects (e.g., temperature and relative humidity [RH] fluctuations in the weighing environment, dust contamination, static charge effects, etc.) and non-laboratory activities (e.g., volatilization of sampled PM, decrease in filter weights due to aging of filter properties) impacting the measured mass of the particles deposited on the filter. Eliminating and/or minimizing these interferences during pre-sampling and post-sampling weighing is critical for a precise calculation of the PM net mass loading and subsequent mass concentration calculation. These controls become even more important for coarse particle ($PM_{10-2.5}$) mass measurements for which the FRM method (U.S.EPA, 2012c) dictates that the coarse PM mass is calculated by subtracting the two PM collections ($PM_{10}$–$PM_{2.5}$) to provide the $PM_{10-2.5}$ mass concentration. For the most precise calculation of the $PM_{10-2.5}$ size fraction, it is imperative that the gravimetric mass determination of both $PM_{10}$ and $PM_{2.5}$ is performed correctly. Error in even one weighing will impact the final mass calculation. In order to ensure precision and accuracy, the FRM method specifies laboratory conditions and quality practices that must be adhered to during the gravimetric mass measurements as specified in the federal regulations (U.S.EPA, 2012a, b, 2013a) and in the Quality Assurance (QA) Handbook (U.S.EPA, 1998, 2013b, 2014). By following the FRM requirements for $PM_{2.5}$ gravimetric analysis (U.S.EPA, 2012b), a laboratory automatically meets the requirements for $PM_{10}$ analysis (U.S.EPA, 2012a) and $PM_{10-2.5}$ (U.S.EPA, 2012c) due to more stringent requirements for the gravimetric analysis of $PM_{2.5}$ filter samples.

It is important to follow the above requirements because for typical ambient samples, the mass of the actual particulate deposit on the filter is negligible (typically < 0.1%) when compared to the mass of the filter material itself. As particulate pollution decreases over time, adhering to the critical and systemic operational criteria will be of great importance in every gravimetry laboratory for accurate measurement. Fig. 1 demonstrates this importance based on more than 10 years of data from samples analyzed in our laboratory. The initial filter weight has remained almost constant, while the net mass collected on the filter (which in turn is a reflection of the particle concentration in the air) has decreased by nearly 29% between 2004 and 2014. Being a non-destructive method, these Teflon® filters used for ambient air monitoring are typically subjected to further chemical speciation analysis, or archived for future evaluation.

Gravimetric measurements can be accomplished using a simple microbalance in controlled laboratory conditions. Robotic weighing systems (RWS) (Ogden *et al.*, 1995) are now available to automate the routine process and reduce human labor, human error, and the cost of the filter weighing procedure. Automated weighing systems have the potential to increase measurement precision for filter weighing, provide lower detection limits for lightly loaded filters, and provide an efficient and low-cost alternative to repetitive manual filter weighing processes. Robotic systems must be evaluated prior to routine use, and periodically thereafter, to ensure no contamination from the robotic mechanical system is deposited on the Teflon® filter.

Previous work has primarily focused on manual gravimetric mass measurements. Feeney *et al.* (1984) discussed approaches used early on to weigh Teflon membrane filters. Tsai *et al.* (2002) discussed the impact of environmental conditions and electrostatic effect on different filter materials and found no impact on Teflon® filters, although our work (as discussed in this paper) shows major impact of static effects. Malm *et al.* (2011) discussed

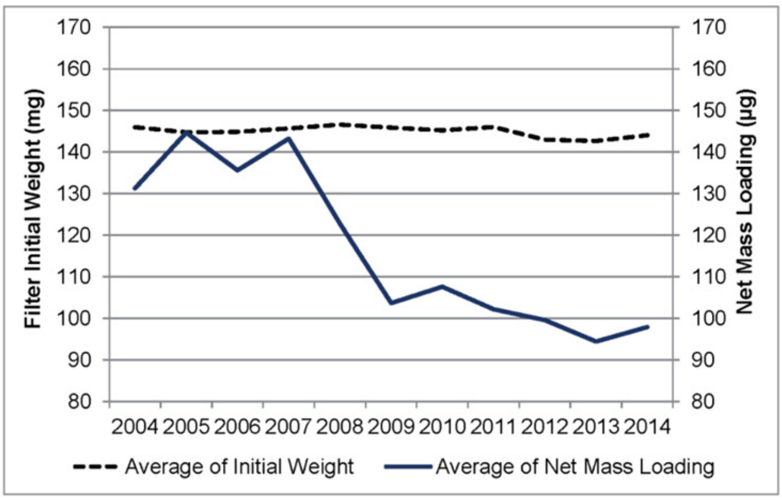


**Fig. 1.** Average net mass loading (in µg/filter, right axis) for the EPA Chemical Speciation Network from 2004 until 2014 illustrating a decline in PM collection while the average initial weight of the Teflon® filter (in mg $filter^{-1}$, left axis) has remained nearly constant.

uncertainties in PM measurements caused by field and sampling artifacts impacting analysis and how these artifacts impacted measurements as part of the two major monitoring networks (Chemical Speciation Network and the Interagency Monitoring of Protected Visual Environments). Lawless and Rodes (1999) discussed approaches to increase data quality for personal exposure samples using manual balances. This paper builds upon the previous work and reports findings specifically related to static effects, improvements to quality practices, and validation of robotic weighing systems that are recently becoming prevalent. Further, our focus in this paper is solely on the measurements in the laboratory and the associated quality practices.

The objectives of this paper are to: 1) briefly review quality practices for accurate gravimetric mass measurements and report quality control (QC) evaluations from several years of analysis; 2) demonstrate the importance of negating electrostatic charges using data from our work; 3) evaluate the performance of a RWS for acceptability and routine measurements; and 4) compare manual and robotic weighing. As part of the evaluation of the RWS, our objective was to further understand the precision capabilities and contamination impacts from fully utilizing a RWS for routine filter weighing while maximizing throughput capabilities and ensuring QC. Specifically, this study analyzed the potential for trace contamination from the RWS or transport carriers that could impact further chemical analysis of the Teflon® filters.

***Quality Practices for Gravimetric Mass Measurements***

The requirements for QA/QC of gravimetric mass measurements have been discussed elsewhere in federal regulations and guidance documents (U.S.EPA, 1998, 2012a, b, c, 2013a, b, 2014). Here, we briefly review those requirements supplemented with experience gained from our work. The method includes tight temperature and humidity controls (20–23°C, 30–40% RH) for filter conditioning and weighing. The strict environmental conditions are required for $PM_{2.5}$ filter conditioning and weighing to ensure a uniform environment for weighing and proper microbalance conditions. Filter conditioning per FRM requirements includes removing an unsampled filter from the box or removing a sampled filter from the field cassette and placing the filter into a petri slide to acclimate to the controlled temperature and humidity conditions in the environmental chambers. Gravimetry of PM samples requires use of an analytical balance with a minimum repeatability of 1 µg, necessitating attention to contamination, environmental conditions, and performance tracking. A QA/QC requirement for documenting microbalance performance is weighing standard reference weights at the beginning, after every 10$^{th}$ filter, and at the end of the weigh session. Tracking debris contamination in the laboratory is achieved through the use of a Laboratory Blank that is included with the initial weigh session and subsequently reweighed during the post-sampled weigh session each time a filter from that initial weigh session is post-weighed. The FRM guidance dictates that one duplicate is required per weigh session, but our experience has shown that a single duplicate does not accurately track issues during a weigh session caused by human movement or error. Further, static electricity buildup cannot be detected from duplicate weighing and can mask data quality issues. A summary of the QA/QC requirements for $PM_{2.5}$ filter weighing detailed in the QA Handbook (U.S.EPA, 2014) is reproduced here as Table 1, to serve as a single collection of the QA/QC checks.

The criteria summarized in Table 1 are the minimum required for valid data for the determination of gravimetric mass in ambient air. With each improvement in the QA/QC criteria detailed in Table 1, person hours (i.e., manual labor) are added to each sample collected, which can make valid data generation considerably expensive for agencies. The accuracy and repeatability of weighing results are impacted by the weighing environment. Technological advances in microanalytical balance electronics have greatly decreased their response times and allowed for easier integration of electronically transmitted data, but have also made the balances even more sensitive to their surroundings. Physical influences that impact the weighing process (vibration, air flow, electrostatic charge, temperature, humidity, etc.) must be understood and controlled.

Electrostatic charge is a persistent problem for the gravimetric analysis of Teflon® filters (Feeney *et al.*, 1984; Weil, 1998). Teflon® is a non-conductive media, which allows for electrical charge accumulation during the weighing process. Static can be induced on the Teflon® filter from the human body, which can then affect the weight of the filter and the performance of the balance. Electrostatic charge is generated through friction between different non-conductive surfaces. Human movement (i.e., an analyst's arm rubbing against the body as one moves a filter onto a weigh pan) makes it difficult to avoid static buildup during a weigh session in the low relative humidity environmental chambers. Teflon® filters can hold an electrostatic charge buildup on the surface creating a bias which might cause duplicates to be within the FRM tolerance despite the weight of the filter not being accurate. Standard weights used to check balance performance are made of metal and therefore do not accumulate static charge and cannot illustrate static generation. Electrostatic discharge (ESD) devices like Polonium strips, ionizing units, and ESD bracelets can assist with removing static from the analyst. Proper body placement and minimal movement during the filter placement on the balance pan can help prevent static charge generation during the manual weighing procedure.

The RTI robotic precision weighing system is equipped with multiple static control devices including Polonium strips and a manufacturer-developed Faraday pan to substantially reduce the effect of static charge on the mass measurement result. In the study presented here, the ability of the RWS to negate static charge and the precision of the RWS in pre-sampled and post-sampled filter weighings were evaluated. The variation in mass measurement between manually and robotically weighed filters was also analyzed. In addition to optimizing the determination of PM in ambient air for NAAQS reporting, the gravimetric analysis will benefit from reduced human effort and the possibility of mental and physical fatigue during filter weighing with increased laboratory throughput and efficiency.

**Table 1.** $PM_{2.5}$ QA/QC Criteria for Gravimetric Measurements (Reproduced from QA Handbook (U.S.EPA, 2014), $PM_{2.5}$ Filter Based Local Conditions Validation Template).

| 1) Criteria ($PM_{2.5}$ LC) | 2) Frequency | 3) Acceptable Range | 4) Reference |
|---|---|---|---|
| CRITICAL CRITERIA- $PM_{2.5}$ Filter Based Local Conditions | | | |
| Filter Conditioning Environment | | | |
| Equilibration | all filters | 24 hours minimum | 1, 2 and 3) 40 CFR Part 50, App.L Sec 8.2.5 |
| Temperature Range | all filters | 24-hour mean 20–23°C | 1, 2 and 3) 40 CFR Part 50, App.L Sec 8.2.1 |
| Temperature Control | all filters | ± 2°C Standard Deviation over 24 hours | 1, 2 and 3) 40 CFR Part 50, App.L Sec 8.2.2 |
| Humidity Range | all filters | 24-hour mean 30%–40% RH or ≤ 5% sampling RH but > 20% RH | 1, 2 and 3) 40 CFR Part 50, App.L Sec 8.2.3 |
| Humidity Control | all filters | ± 5% Standard Deviation over 24 hours. | 1, 2 and 3) 40 CFR Part 50, App.L Sec 8.2.4 |
| Pre/post Sampling RH | all filters | difference in 24-hour means ≤ ± 5% RH | 1, 2 and 3) 40 CFR Part 50, App.L Sec 8.3.3 |
| Lab QC Checks | | | |
| Lab Filter Blank | 10% or 1 per weighing session | ±15 µg change between weighings | 1) 40 CFR Part 50, App.L Sec 8.3.7.2 2 and 3) Method 2.12 Sec. 7.7 |
| Balance Check (working standards) | beginning, $10^{th}$ sample, end | ≤ ± 3 µg | 1, 2 and 3) Method 2.12 Sec. 7.9 |
| Duplicate Filter Weighing | 1 per weighing session | ± 15 µg change between weighings | 1, 2 and 3) Method 2.12 Sec 7.11 |

## METHODS

### *Description of the Gravimetry Laboratory*

Filter weighings performed in this study were completed in the RTI International environmental chamber dedicated to filter-based air samples also referred to interchangeably as the "environmental chamber" or "chamber." The Gravimetry Laboratory is a self-contained, climate-controlled 4 m × 4.6 m chamber with design performance-rated for temperature uniformity of ± 1°C and RH uniformity of ± 5% RH. Laboratory temperature and humidity are monitored continuously by the chamber's master system installed and maintained by Bahnson Environmental Specialties (Raleigh, NC). The environmental chambers were designed to minimize chances of dust entering the chamber environment and provide the optimal environment for analyzing filter media. Temperature and humidity are maintained to a 24-hour mean temperature of 20°C to 23°C with a ± 2°C standard deviation and a 24-hour mean RH of 30% to 40% with a ± 5% standard deviation. The chamber's RH set points and control systems are maintained to meet the FRM requirement that the pre-sampled and post-sampled conditions are within < ±5 % RH. The temperature and RH are continuously measured with Vaisala (Boulder, CO) data loggers, which are monitored by laboratory analysts before, during, and after filter weigh sessions. The data logger used for long term tracking of the environmental chamber provides historical information on the chamber performance (See Supplemental Material Fig. S1). The FRM criteria are met by never performing weighing activities when the chamber temperature and humidity specifications are outside the requirements detailed here. This ensures the conditioning environment meets specifications for the filter media and is a suitable environment for sensitive electronics of the microanalytical balances. The positive-pressure chambers are equipped with both high-efficiency particulate air (HEPA) and charcoal filtration and dedicated to the inspection, conditioning, and weighing of air sampling filters preventing contamination from bulk sample materials. Filter integrity is ensured with limited/controlled sample handling for inspection, conditioning, and weighing filters in the same controlled environment. Monitoring the chamber environments, balance performance, and laboratory cleanliness to meet the minimum of the requirements of the FRM guidelines results in the most stable filter weighings and the most accurate net mass determination in ambient air.

### *Microbalance Specifications*

The laboratory includes both RWS and stand-alone microbalances. The RWS consists of the MTL Corporation AH-225 Precision Weighing System (Minneapolis, MN). This RWS features instrument specifications including a repeatability of 0.75 µg for filters and 0.25 µg for check standards and static discharge prior to and during filter weighing using Po-210 and MTL's internally-developed Faraday pan. The RWS utilizes a Vaisala HMT-333 data logger to perform continuous environmental monitoring of the environmental chamber. The RWS microbalance is a Mettler Toledo XP6 (Columbus, OH) with a readability of

1 µg and repeatability of 0.8 µg. The Filter Weighing System software is Version 3.0.5 and is used to control the entire weighing process. The RWS is linked to a computer database and records data collected by the autohandler system, including balance readings, environmental readings, time of day, operator of system, and QC procedures.

The stand-alone analytical microbalances used for manual weight determinations are Mettler Toledo (UM and XP Series Microbalances) with a readability of 0.1 µg and a repeatability of 0.25 µg and Sartorius microbalances (Cubis Series Microbalances) (Bohemia, NY) with readability and repeatability of 1 µg, which are equipped with multiple static charge protections. Each microbalance is linked to a computer to allow the weighing data to be transmitted automatically to a database.

### *Mass Measurements*

Our process for both manual and automated weighing with the RWS for both pre-sampling (tare) and post-sampling (exposed) filters follows the FRM (U.S.EPA, 2012b, a, c, 2013a) and QA handbook guidance (U.S.EPA, 1998, 2013b, 2014).

All filter weighings were completed using Whatman (GE Health Care, Pittsburgh, PA) and MTL (MTL Corporation, Minneapolis, MN) Teflon® 47-mm filters with an EPA-specified FRM acceptance limit of less than 5 µg total mass change in tare weight of 10 filters over a 24 hour period. Filters were allowed to condition for a minimum of 24 hours in the environmental chambers to acclimate to the temperature and RH prior to weighing. The sampled filters that were analyzed in this study had been collected as part of the EPA $PM_{2.5}$ Chemical Speciation Network. In the RTI Gravimetry Laboratory, all filters that can be placed on the balance pan are post-weighed despite defects or filter damage and were used in this study. A filter with defects or damage was flagged appropriately in the database. Only filters with a hole large enough to prevent placement on the balance pan are archived with no post weight. All standard weights used by the RWS were designed, manufactured, and annually-certified by Heusser Neweigh (Bay Point, CA) ISO 17025 Accredited Calibration Services, accredited by the American Association for Laboratory Analysis (A2LA) to ISO/IEC 17025:2005 under certificate 1823.01. Standard weights used for manual weighing are annually certified by Troemner (Thorofare, NJ), accredited by the National Voluntary Laboratory Accreditation Program (NVLAP) to ISO/IEC 17025:2005 under lab code 105013-0.

### *Performance Evaluation of the RWS*

Evaluation of the RWS began by robotically weighing filters that were also manually weighed as the RWS was brought online. Upon verification of the RWS performance, unsampled filter weighing began with 100% duplicate QC to track the precision performance of the RWS. When filters were returned from sampling sites, they were also post-weighed with 100% duplicates performed to ensure high quality data and track the precision performance of the RWS. Over 10,000 weighings were performed to evaluate the RWS. Critical factors impacting QC such as static effects and potential for contamination were especially considered in the analysis. In addition to evaluation of the RWS precision, a comparison of the RWS to manual weighing was completed.

To analyze the potential for trace metal contamination of the RWS silos (see Supplemental Material Fig. S2 for definition), filters were kept in transport carriers in the RWS for increasing lengths of time (24, 48, 84 and 108 hours). The filters were then weighed every 24 hours using the filter weighing procedure. Filters were run on the RWS for varying lengths of time that were longer than what is required for FRM valid mass data. The longer lengths of time are not typical for the fast turnaround analysis time in a PM gravimetry laboratory, but the authors wanted to determine if residence time had any impact on elemental contamination in the event of an episode that prevented the filter from being unloaded from the RWS. Trace metal contamination analysis was performed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) completed on a Thermo Fisher Scientific, Inc. (Waltham, MA) X-Series II with collision cell. The ICP-MS Extraction was done by the federal equivalent method EQL-0510-191 (Weber *et al.*, 2010; U.S.EPA, 2015).

The metals chosen for analysis were the National Air Toxics Trends Station (NATTS) suite of elements to ensure all filters analyzed by the RWS could be subsequently analyzed for air toxics regulated under the CAA and/or used for other chemical speciation analysis such as X-ray Fluorescence. Ten hazardous air pollutants (HAPs), or air toxics, regulated under the CAA were analyzed in this study. HAPs have been associated with a wide variety of adverse health effects, including cancer and neurological effects. The NATTS program provides long-term HAP monitoring data of consistent quality illustrating the need to ensure no contamination would be caused by the RWS. The detection limit for each metal was 0.250 ng $mL^{-1}$. For an extraction volume of 20 mL, this calculates to 5 ng $filter^{-1}$.

### *Project Analysis Techniques*

The RWS "direct read weighing" procedure, a setting in the RWS, was used for analyzing over 1,500 unsampled and sampled filters that had also been manually weighed to determine the net mass loading of PM on the filter. The direct read weighing procedure setting is the system's closest procedure to a manual weighing process while still eliminating the human movement component to the process. The robotic arm retrieves the filter in the transport carrier from a holding silo and places the filter on the balance pan (see Supplementary Material Fig. S2). The RWS software tares the balance prior to opening the weighing chamber, and then, it waits 30 seconds for a stable balance reading. The robotic arm then removes the filter and places the filter and carrier back into the holding silo. The RWS is set to weigh the dedicated standard weights and lab blanks as the FRM guidance dictates. The only procedural difference between the robotic and manual weighing process is that the RWS is set to 100% duplicates to ensure data precision compared to a maximum of 30% duplicates in manual weighing. An advantage of robotic weighing is that the 100% duplicate check is possible with no additional human effort required.

In a separate demonstration of the RWS, a single, unsampled filter was utilized to collect continuous data by weighing it repeatedly for 72 hours. Per the FRM guidance, standard weights were weighed after every tenth filter weight. This continuous weighing allowed evaluation of the RWS precision in a manner that could never be completed by a human analyst. Long term analysis of lab blanks kept in the RWS for every weigh session also provides validation of the RWS precision.

## RESULTS AND DISCUSSION

### *Trace Metal Contamination Evaluation in the RWS*

The trace metal concentrations for the Teflon® filters analyzed by ICP-MS is shown in Supplementary Material Fig. S3. The ICP-MS filter results were averaged as sets for each length of time the filters were analyzed in the RWS. Experiments with 24 hour exposure were repeated three times (referred to as Sets 1, 2, and 3). Sets 1 and 2 had a blank filter (referred to as 0 Hours). Analysis for filter sets in the RWS for 0–48 hours had 3 filters, while analysis for the group of filters in the RWS for 84 and 108 hours had 5 filters in the set. Supplementary Material Fig. S3 illustrates that no metals in the analysis suite were above the detection limit of 5 ng filter$^{-1}$ indicating no significant trace metal contamination attributable to the carriers or RWS movements. The trace metal concentrations for the blank filter (0 hours) were similar to the loadings found for the study filters. This indicates that the trace metal loadings found on the filters were typical of levels on blank Teflon® filters. While some variability is seen for Nickel and Manganese, the values are in the noise range being below the detection limit. Regardless, this may suggest the need for periodic (e.g., annual) checking as part of routine QA/QC to ensure that metal coatings on the RWS do not wear off with continued operation over time.

### *Precision of Robotic Weighing*

For over 7,000 routine unsampled and sampled unique filters, duplicate weighings obtained by the RWS showed that 81% of the absolute differences were within 0–3 µg in the environmental chambers (Fig. 2(a)). Maintaining FRM environmental specifications can cause chamber air flow that can disrupt the sensitive electronics in environmental chambers required for weighing precision for both manual and robotic weighing. The RWS procedure was set to weigh as closely to manual weighing as possible using just the single, direct read setting, which provides the level of precision that would be seen in manual weighing. This method of robotic weighing would also evaluate how the RWS performed with no reduction in chamber fan speed or additional air flow protection. In addition, the RWS has additional procedure capabilities to further increase the precision that include substitution weighing and triplicate weighing. The performance of the replicate weighings in Fig. 2(a) illustrates the stability of the RWS in the chamber environment. For over 10,000 weighings, the RWS never resulted in a replicate that was outside the FRM specification of ± 15 µg. The distribution also shows a bell-shaped curve

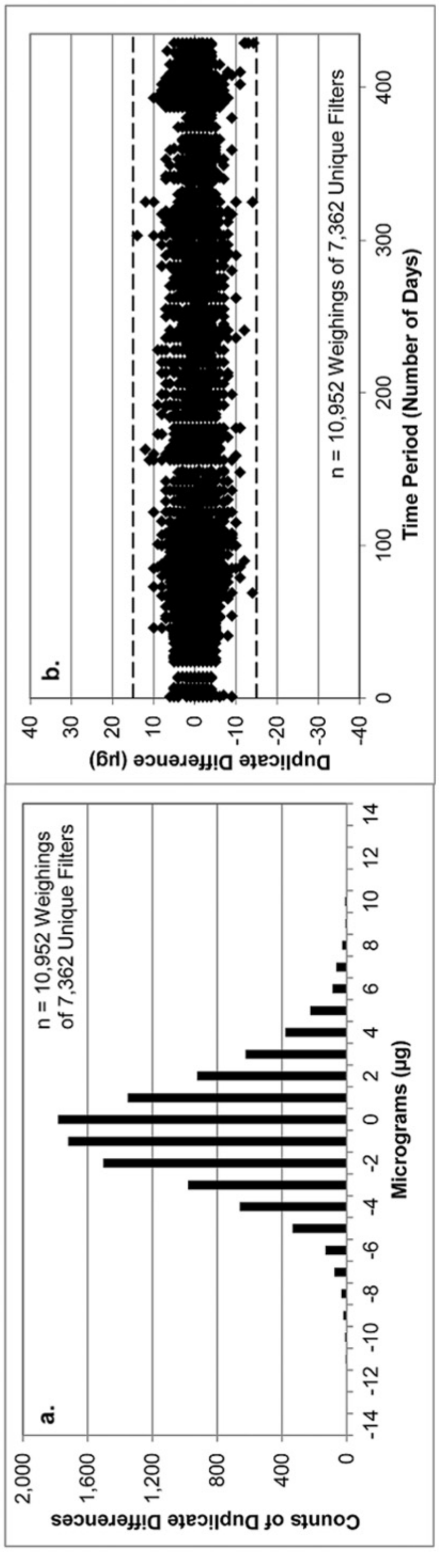


**Fig. 2.** RWS duplicate weighings of more than 7,000 filters: (a) distribution of differences between weights and (b) variation of differences over time.

demonstrating no specific bias in duplicate measurements. Fig. 2(b) demonstrates the stability of the precision over time. The environmental chambers maintain positive air pressure so that when the door is opened and closed it can momentarily increase air flow disrupting the stability of the sensitive microbalances. While the robotic system can be run at times when analysts are not there, this was not dictated during these weighing procedures to evaluate how the RWS would fit into laboratory daily activities. Figs. 2(a) and 2(b) substantiate the precision of the robotic weighing system, which exceeds the requirements for implementation into a gravimetry laboratory. Based on replicate weighings over a year of robotically weighed unsampled and sampled filters, the precision of the RWS is estimated to be 3 µg for both pre- and post-sampled filter weighings. These were calculated using the standard deviation of the replicate mass difference as recommended by QA Handbook (U.S.EPA, 1998, 2013b, 2014). The average of the differences for that year was –0.32 µg and –0.74 µg for pre- and post-sampled filters, respectively. The RWS precision for the net mass loading, calculated as the square root of the sum of the squares of the pre- and post-sampled standard deviation of replicate weighings, is 4 µg.

In addition to the evaluation for trace metal contamination, a historical look at Laboratory Blank weighings also provided insight into both particulate contamination in the RWS and precision performance over time. Laboratory Blanks were used to track debris contamination in the environmental chamber. A Laboratory Blank is created at the time of the tare weighing session and is then reweighed each time a filter from that weigh session is post-weighed. In between the weighings, the Laboratory Blank is kept in a petri slide with the lid partially open as a passive debris sample collector in the environmental chamber. The RWS was also able to weigh a Laboratory Blank every weigh session with no additional analyst labor to show longer term debris tracking. In Fig. 3, the over 1,400 weighings of 243 lab blanks show only 4 times where the net mass difference was +15 µg over the initial weighing of the lab blank. These 4 weighings were for 2 laboratory blanks, which had been weighed several times over the span of more than two months. This verifies robotically weighed filters are no more inclined to particulate contamination in the Gravimetry Laboratory than manually weighed filters. This stability in multiple weighings of the same filter further illustrates that precision of the RWS, where 50 of the 243 filters were weighed 10 or more times.

***Repeatability for Continual Weighing***

The repetitive high precision capabilities of the RWS are illustrated in Fig. 4 through the analysis of a single filter weighed over a three-day period. The standard weights were weighed after every 10 filter weights and show no change in net mass difference (See Supplemental Material Fig. S4). The standard deviations of the groups of 10 filter weights show no statistically significant change from the first group and last group of weighings shown in Fig. 4. The collection of filter weights (Supplemental Fig. S4) by the RWS showed negligible drift between the first and last time the filter was weighed, which is attributed to the filter media stability and not the RWS based on the fact that standard deviation of sets of filter weights showed no such drift. This performance shows the RWS can consistently and repeatedly weigh filters for days with high precision showing no drift in weighing performance or effects of static. The repeated weighing of the single filter also allowed for a precision calculation of the RWS using the filter weights over time. The standard deviation of the repeated filter weights over the three day period was 2 µg, demonstrating excellent precision.

***Comparison to Manual***

Reducing the impact of static electricity on filter weighing is a continuous concern in a gravimetry laboratory (Weil, 1998). The generation of static charge on a Teflon® filter is difficult to detect during a weighing session as static charge can remain on a filter during the replicate weighing. This implies that even duplicate weighings performed on the same day may not identify this impact. In addition to being

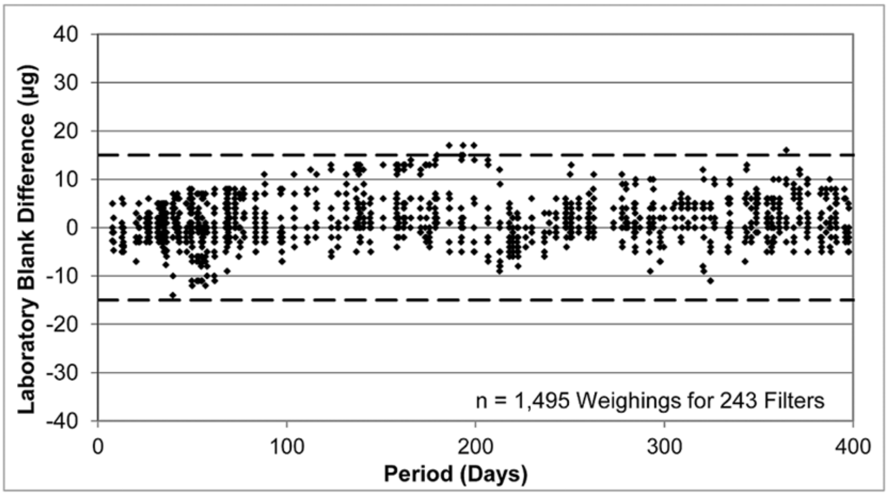


**Fig. 3.** Laboratory Blank weighings for a period of 400 days illustrating 1,491 weighings within the FRM speciation of ±15 µg.

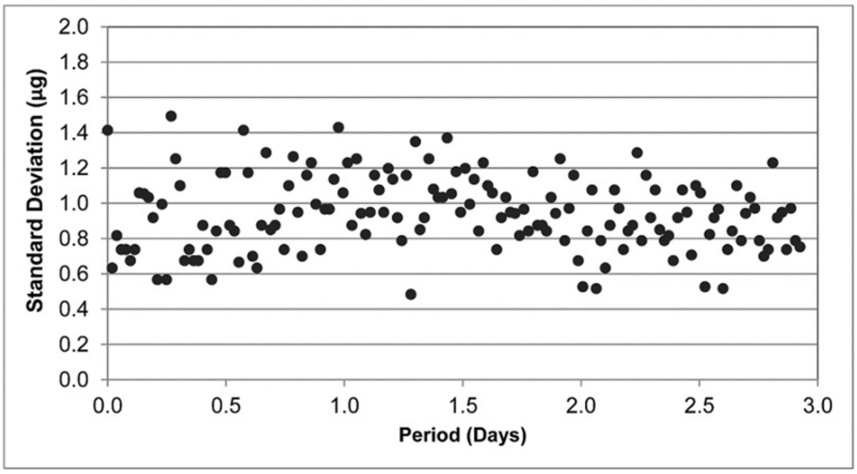


**Fig. 4.** Standard Deviation for groups of 10-filter weights for a single filter weighed continuously over a three day period.

influenced by cold temperatures and low humidity, the effect of electrostatic charge is also analyst-dependent. We present here data from our experience that demonstrates the impact of static charge on filter mass loadings. Our experience has shown that static charge can affect individual analysts and remain on a Teflon® filter at least overnight, emphasizing the need for a weighing process that is free of electrostatic charge. This issue was thoroughly investigated and studied to determine and negate the tendency for humans to impart static on Teflon® filters. Figs. 5 and 6 demonstrate the impact of static on filter mass loadings as a function of analyst. In these figures, analyst A represents an analyst with a tendency to attract high electrostatic charge, while analysts B and C refer to other analysts with low to normal tendency.

Fig. 5 provides an example of a Laboratory Blank filter that was weighed by analyst B with no net mass difference, but when it was weighed by analyst A, the Lab Blank showed a positive mass difference around 15 µg. This type of impact was observed on multiple instances for lab blanks as well as for duplicate weighings. Based on our research, it was found that if another analyst B weighed a batch of filters prior to and after analyst A not only were analyst A's weights much higher than analyst B, but if also weighed after analyst A, the filter weights became unstable and would gradually decrease in weight until they approached the original weights of analyst B as seen in Fig. 6. This process was repeated over three times where the filters were let to sit at the Haug static ionizer (Mississauga, ON, Canada) after analyst A's weighing and each time showed the same pattern. This process led to the discovery that analyst A was building up an electrostatic charge, which was getting transferred to the filters. Over time, the filters very slowly discharged the electrostatic charge, manifesting itself as loss of weight when weighed by another analyst.

After the realization that static electricity was the most likely culprit of the high weighings (Fig. 6) and the subsequent confirmatory test to illustrate the static effects (See Supplemental Material Fig. S5), multiple static protections were evaluated by the analyst, and weighing checks were implemented to detect and eliminate static issues. Additional ESD protections were taken to dissipate this static charge buildup so that it did not affect the filter weighing results.

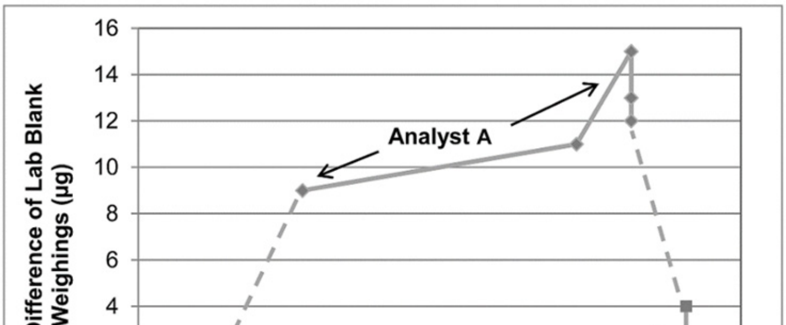


**Fig. 5.** Laboratory Blank weighings demonstrating Analyst A imparting static on Teflon® filter.

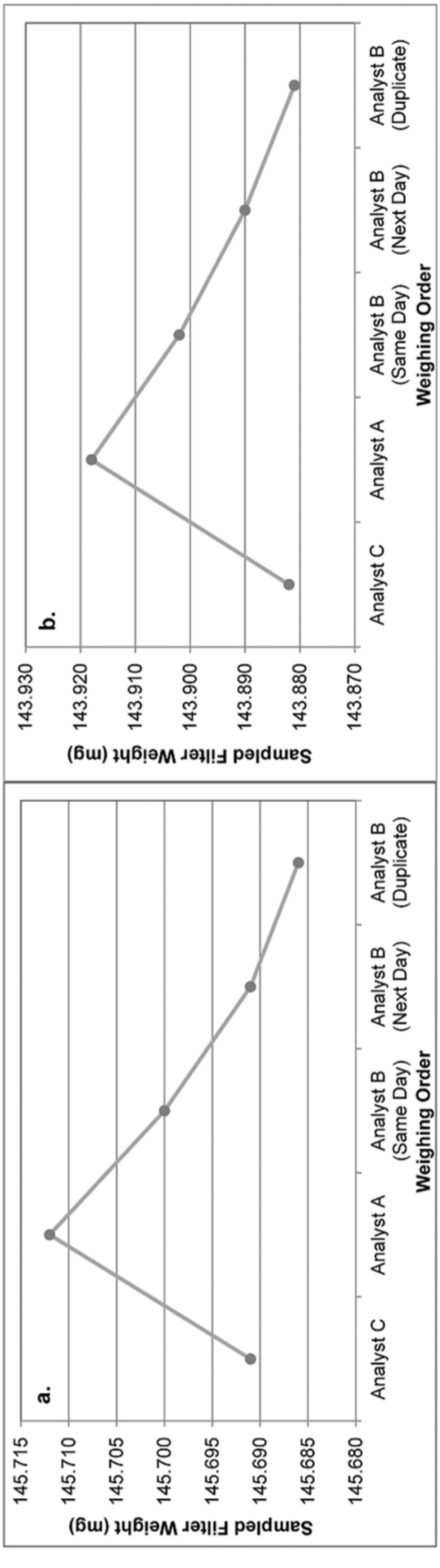


**Fig. 6.** Experiments designed to determine the cause of the high Laboratory Blank weighings seen in Fig. 5. A sampled filter weighed first by Analyst C showed an increase in filter weight when measured by Analyst A, and then decreased back to original final weight when measured by other analysts.

After an evaluation of methods, ESD bracelets and grounding monitors were found to be the most effective. In addition, anti-static lab coats provided better protection than the previously used personal protective clothing/lab coats.

Additional checks are also required as part of data review. Data reviewers should watch for Laboratory Blanks that randomly increase and decrease in net mass differences. QC charts should be evaluated by analyst performance to show tendencies to have Laboratory Blanks outside FRM specifications (Table 2) and replicates out of tolerance. Table 2 presents an example of tracking Laboratory Blanks before and after the implementation of additional static protections. Additional static protections (Polonium 210, static control lab coats, and ESD grounding wrist straps with a ground monitor) were implemented in 2011 after the discovery of static effects during 2010. For the manually weighed filters during 2010, 32 weighings of 21 unique Laboratory Blank filters showed the static effect illustrated in Fig. 5 with net mass differences across the 21 unique filters ranging from –55 to –18 µg and 20 to 46 µg. All but one of the unique filters with net mass differences outside the ± 15 µg acceptance limit were associated with either an initial or post weighing by analyst A who exhibited the increased static effects. If another analyst re-weighed a Laboratory Blank initially tare weighed by analyst A, the net mass difference was predominately negative resulting in the –54 and –55 µg net mass differences seen in Table 2. When Laboratory Blanks not weighed by analyst A were weighed by any combination of the other analysts, the net mass differences were within specification further illustrating static effects on the Laboratory Blank weights. A comparison of Laboratory Blanks weighed in 2010 including and excluding analyst A is shown in Supplementary Material Table ST1. Our work revealed that Laboratory Blanks were the best approach with a higher probability of success over duplicate weighings to detect static. This is because static charge can stay on the Teflon® filter over duplicate weighings, and therefore, not be detected as an anomaly. Despite these additional protections, this extreme case of static charge shows the difficulty in pinpointing static effects indicating that removing the predisposition of human movement to build static charge on a Teflon® filter is invaluable to filter weighing results.

Fig. 7 shows the net mass difference between unsampled filters (7a) and sampled filters (7b) weighed both manually and robotically. For both filter types, the manually weighed filters are significantly more likely to have a higher filter weight over a robotically weighed filter. While the difference for unsampled filters is commonly within the tolerance of the FRM (± 15 µg), the higher manual weights are attributed to the effect of electrostatic charge. This effect is seen more prominently with sampled filters where the difference was at the duplicate specification of + 15 µg and even approached the specification of field blanks (± 30 µg), which illustrates that electrostatic charge for manually weighed filters could be an issue for lightly loaded filters and may bias the estimate of the mass deposited on the filter. This also illustrates that manual weighing static effects cannot be completely eliminated, but can be minimized through ESD protections.

**Table 2.** Laboratory Blank QC tracking by analyst shows improvements in QC through additional static protections (Polonium 210, static control lab coats, and ESD grounding wrist straps with a ground monitor) implemented in 2011.

| Analyst: | Analyst A | Analyst B | Analyst C | Analyst D | Analyst E | Total |
|---|---|---|---|---|---|---|
| | | | 2010 | | | |
| Count | 616 | 519 | 57 | 338 | 497 | 2,027 |
| Avg | 2.75 | 2.8 | 3.37 | 0.49 | 1.42 | 2.08 |
| Max | 20 | 26 | 9 | 11 | 46 | 46 |
| Min | –41 | –29 | –4 | –54 | –55 | –55 |
| Range | 61 | 55 | 13 | 65 | 101 | 101 |
| Std Dev | 5.11 | 4.77 | 3.43 | 6.72 | 5.89 | 5.56 |
| # Out | 4 | 9 | 0 | 11 | 8 | 32 |
| % Out | 0.60% | 1.70% | 0.00% | 3.30% | 1.60% | 1.6% |
| | | | 2011 | | | |
| Count | 436 | 587 | 42 | 463 | 506 | 2,034 |
| Avg | 0.94 | 1.69 | 1.43 | 1.24 | 0.8 | 1.2 |
| Max | 12 | 14 | 11 | 13 | 12 | 14 |
| Min | –10 | –9 | –9 | –18 | –19 | –19 |
| Range | 22 | 23 | 20 | 31 | 31 | 33 |
| Std Dev | 3.57 | 3.39 | 4.56 | 4 | 4.2 | 3.82 |
| # Out | 0 | 0 | 0 | 1 | 2 | 3 |
| % Out | 0.00% | 0.00% | 0.00% | 0.20% | 0.40% | 0.10% |
| | | | 2012 | | | |
| Count | 809 | 430 | 61 | 379 | 390 | 2,069 |
| Avg | 1.45 | 4.27 | 2.31 | 2.92 | 0.92 | 2.24 |
| Max | 16 | 31 | 12 | 13 | 14 | 31 |
| Min | –13 | –6 | –7 | –12 | –10 | –13 |
| Range | 29 | 37 | 19 | 25 | 24 | 44 |
| Std Dev | 4.26 | 5.03 | 4.11 | 4.35 | 3.97 | 4.56 |
| # Out | 1 | 3 | 0 | 0 | 0 | 4 |
| % Out | 0.10% | 0.70% | 0.00% | 0.00% | 0.00% | 0.20% |

# Out and % Out refer to the number and percent of observations, respectively, outside the acceptance limit of ± 15 µg.

Interlaboratory comparison evaluations are an integral QA test to evaluate a laboratory's performance for determining the gravimetric mass of a PM filter sample. The National Analytical Radiation Environmental Laboratory (NAREL) administers a Performance Test (PT) annually to evaluate laboratories providing analysis support to the EPA. In this PT, the facilities and Standard Operating Procedures employed for the gravimetric determination of PM samples were to be utilized to equilibrate and determine the mass of 10 Teflon® filters by obtaining a tare weight for the filters and sending them back to the NAREL where they were used in a sampler to capture $PM_{2.5}$. The sampled filters were then returned to determine the final post-weight and subsequent $PM_{2.5}$ mass captured on the filter. In 2014, the Gravimetry Laboratory utilized the PT to evaluate the RWS against manually weighed filters at both RTI and at NAREL. In Fig. 8, the tendency for higher tare- and post-weights for manually weighed filters is shown, but it also shows that this effect is lessened in the net mass loading calculation. Both robotically weighed and manually weighed filters resulted in net mass loadings that were within the PT advisory limits of –0.016 µg to 0.018 µg difference to NAREL. Thus, even though static charge may impact manual weighings more than the RWS process, the impact is likely to be minimal if the same analyst performs both pre and post weighing along with enhanced static control measures. However, given the dependence of static buildup on environmental conditions as well as human-related characteristics/factors (e.g., clothing material, skin moisture, etc.) and movement, variability in static impact even for a same analyst cannot be excluded, resulting in potentially biased estimates of mass. These results underscore the importance of implementing procedures and measures to eliminate static.

As an example of tracking QC measures over time, Table 3 summarizes the yearly QC metrics for Laboratory Blanks from manually weighed filters from 2008–2013 as well as the Laboratory Blanks weighed by the RWS. The variability in manually weighed filters is evident through the years including the issue of static identified and rectified in 2010. From 2011–2013, closer tracking of QC criteria made a difference in the number of filters that were out of tolerance, but this also resulted in higher labor hours to ensure this quality of data. Over the year that the RWS was employed, the Laboratory Blanks were loaded into the RWS per the procedure but no extra effort had to be taken to monitor the Laboratory Blank results.

In the comparison of Laboratory Blanks in Table 3, the maximum and minimums for manually weighed filters are slightly higher than the robotically weighed Laboratory Blanks. Manually weighed Laboratory Blank ranges ranged from 51 µg to 101 µg with limited static protections and from 33 to 44 µg with additional static controls, compared

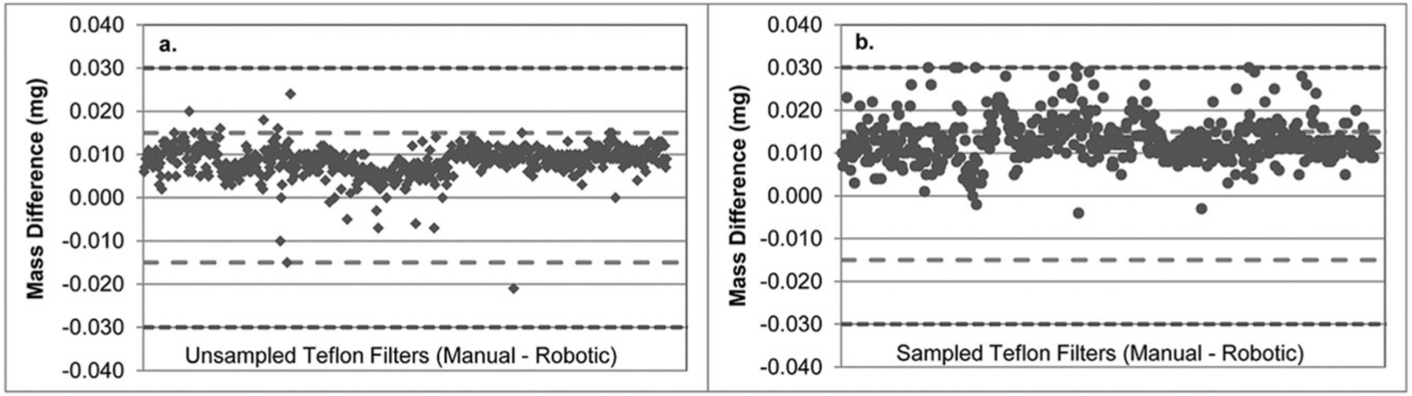


**Fig. 7.** Mass difference between manual and robotic weighings for (a) unsampled and (b) sampled Teflon filters.

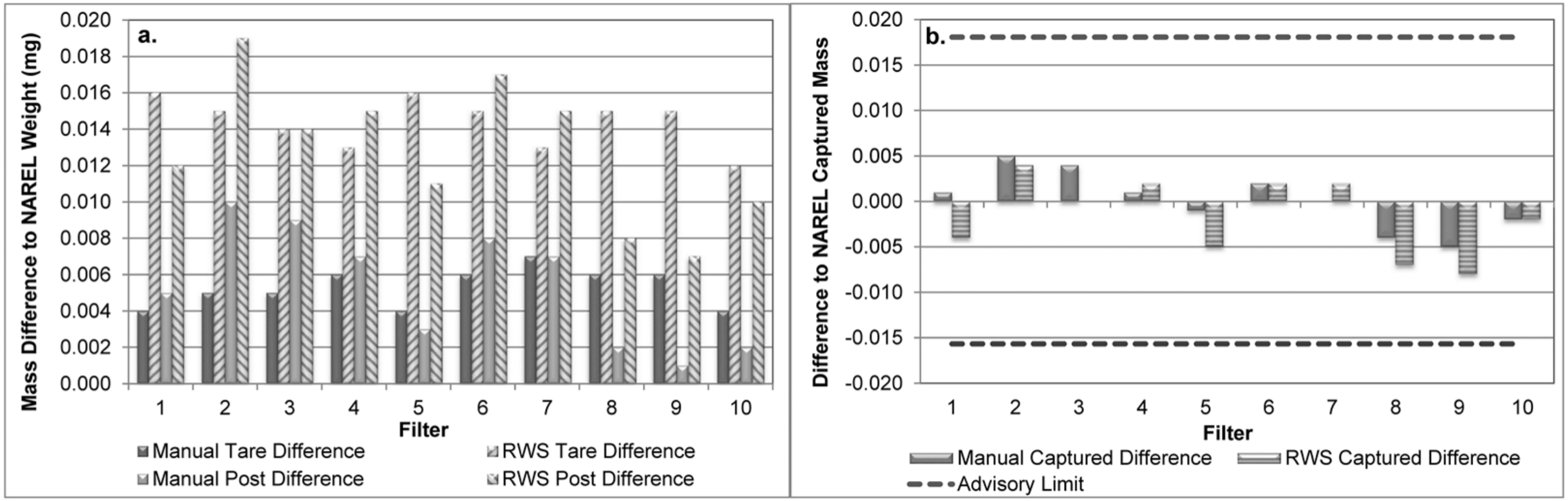


**Fig. 8.** NAREL Performance Test (PT) Comparisons for RWS and manual weighings: (a) difference in measured mass between NAREL and RTI for tare weighing and post-weighing and (b) difference in the net captured mass.

**Table 3.** Yearly QC charting for Laboratory Blanks from manually weighed filters from 2008–2013 illustrating their variability compared to RWS.

| Method | 2014–2015 | 2008 | 2009 | 2010 | 2011 | 2012 | 2013 |
|---|---|---|---|---|---|---|---|
| | RWS | MANUAL | MANUAL | MANUAL | MANUAL | MANUAL | MANUAL |
| Count | 1379 | 1766 | 1864 | 2027 | 2034 | 2085 | 1874 |
| Avg | 1.71 | 2.6 | 3.05 | 2.08 | 1.2 | 2.31 | 1.61 |
| Max | 17 | 20 | 31 | 46 | 14 | 31 | 27 |
| Min | –14 | –15 | –20 | –55 | –19 | –13 | –9 |
| Range | 31 | 35 | 51 | 101 | 33 | 44 | 36 |
| Std Dev | 4.81 | 3.85 | 3.98 | 5.56 | 3.82 | 4.62 | 3.85 |
| # Out | 4 | 6 | 18 | 32 | 3 | 4 | 3 |
| % Out | 0.30% | 0.30% | 1.00% | 1.60% | 0.10% | 0.20% | 0.20% |

# Out and % Out refer to the number and percent of observations, respectively, outside the acceptance limit of ± 15 µg.

to a range of 31 µg for the RWS. The highly variable Laboratory Blank net mass differences in Tables 2, 3, and ST1 are not seen when utilizing robotic weighing not only because of the decrease in static effects but because the single instrument is weighing all filters, not multiple individuals.

The FRM Duplicate Filter Weighing requirement is 1 filter per weighing session and a tolerance specification of ± 15 µg change between weighings. Our experience with data validation and the chances of human error, static charge, and filter media effects in filter weighing QC led to more stringent quality procedures in the RTI Gravimetry Laboratory as seen in Table 2. To better ensure valid data for the determination of PM on Teflon® filters, RTI operating procedures implemented prior to 2008 established a ± 5 µg duplicate tolerance and a minimum of 10% replicate weighings in a weigh session. This level of quality assurance provides a high level of precision in manual weighing at RTI, but also increases the human effort involved in the analysis. A histogram of the mass difference from 0 to 5 µg (normalized to the total number of weighings) of robotically and manually weighed tared and post-sampled filters can be seen in Supplemental Material Fig. S6. If analysts follow QC procedures that are more stringent than prescribed by FRM, there is no statistically relevant difference between the precision between the analysts and RWS. However, there is a considerable human labor savings in robotically weighed filters to achieve this level of precision. For example, it took 3.9 minutes per filter following FRM QC and a more stringent 30% duplicates (on average) requirements. This was calculated by taking the total time analysts spent weighing filters for a year and dividing that time by the total number of filters weighed. This time of 3.9 minutes is all analyst labor activity, while the RWS weighed filters in an average of 2.2 minutes per filter instrument time at all QC percentage levels. In comparison to the human effort for a manual weigh session at 30% duplicate percentage, time savings achieved by robotically weighing filters would allow more filters weighed per hour for no analyst labor time with an increase in quality in the duplicate percentage and static control. Note that during the robotic weighing session, the only human effort involved is loading and unloading the robotic system and setting the procedure in the software (on the order of an estimated 1 minute per filter).

## CONCLUSIONS

Gravimetric mass measurements are a simple process, but highly susceptible to bias during the filter weighing procedure. Mass measurements need to be performed under controlled specified laboratory conditions to meet accuracy and precision specifications. This is essential to tracking long term trends and changes in air quality. Our experience has shown that electrostatic charge impacts may be hard to detect. Tracking of laboratory blanks weighed by different analysts over a long period of time was found to be the best way to identify static impacts. Duplicate weighings were not effective, particularly when performed in the same weighing batch, as electrostatic charge tends to dissipate from Teflon® filters at a slow pace. Stringent measures are needed to negate the impact of static.

The RWS showed a high degree of precision and accuracy, evidenced by no change in standard weights and negligible drift (2 µg standard deviation) in filter weight for repetitive weighing of a single filter over a three day period. Relative to the manual weighing, the RWS was found to be minimally impacted by static. Trace metals analysis of filters placed in the RWS for NATTS metals showed no contamination of filters even when weighed robotically over a period of over 100 hours. Laboratory Blank results also indicate there is no additional risk to debris contamination for robotically weighed filters relative to manually weighed filters.

Historically, to ensure valid data of the highest quality, RTI developed manual weighing QC procedures to achieve data with a high level of precision with specifications more stringent than the requirements dictated by the FRM. Adherence to these more stringent specifications show that the precision level between manually and robotically weighed Teflon® filters is equal. However, the human effort required to achieve this is considerable making the RWS high throughput and high precision a benefit for filter based gravimetric analysis. Based on the estimated human effort involved in robotic and manual weighing, robotic weighing provides approximately 75% time savings over manual weighing. Manual weighing has an increased static effect potential with each human movement and as indicated here can occur suddenly in weighing results that are hard to realize. Results from this study show robotic weighing results are better able to control static effects during filter weighing, but independent assessment of accuracy through PT analysis illustrates net mass loadings agree between the manual and RWS. The RWS has the additional confidence of 100% duplicate weighing at no additional human labor hours providing assurance in weighing results. In addition, the RWS can complete weighings with increased precision such as triplicate weighing and substitution weighing for indoor and other low loading samples.

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## SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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